

Innovative Nano-TiO₂ Particles for Self-cleaning Treatments of Historic Architecture and Sculptures

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Abstract

The study reports the results of a new treatment based on water and ethylene glycol nano-TiO₂ dispersions showing photocatalytic properties that was tested on both Noto stone (calcarenite) and Carrara marble. To verify that the proposed treatments did not affect the intrinsic properties of the stone materials, colour measurement, static contact angle and water absorption by capillarity tests were carried out before and after the treatments. The efficacy of the photocatalytic activity of TiO₂ nanoparticles applied to the stone substrates was evaluated by decomposition tests of organic colorants (Rhodamine B), both after indoor natural light exposition and after ageing in a Xenon lamp solar box. The specimens were also exposed to outdoors environment in order to verify their properties as self-cleaning agents to prevent soiling. The results showed that nano-TiO₂ dispersions were effective and suitable for the use in the field of architectural heritage.

Keywords: Nano-TiO₂; Self-cleaning treatment; Stone conservation; Architectural heritage.

1 Introduction

In order to improve the consolidation and/or protection performance of restoration materials, different nanoparticles were added to these materials in order to reduce cracking and maintain their transparency. Different strategies were implemented, such as applying dispersions of alkaline earth metal hydroxide nanoparticles or adding nanostructured SiO₂, Al₂O₃, TiO₂ in low and high molecular weight matrices [1, 2].

During the last decade, a considerable part of scientific research was devoted to the synthesis of innovative coatings based on TiO₂ nanoparticles, which are employed to solve environmental problems regarding the purification of water and air from harmful compounds produced by industries, heating systems and traffic. The photocatalytic activity of TiO₂ prevents the accumulation of deposits by inducing the decomposition of polluting agents, either organic or inorganic, thus improving the protection of masonries from soiling processes. Moreover, TiO₂ nanoparticles increase the wettability of the surface on which they are applied giving rise to the so called “self-cleaning” effect [3, 4], so that any deposits are easily washed away by rain and condensation water.

Commercial TiO₂-based coatings have several important limitations for the application in the cultural heritage field. Most of them require to be irradiated by an ultraviolet (UV) light source, in order to activate the TiO₂, and are not effective in normal outdoor conditions. Furthermore, they may change the aesthetic aspect of surfaces due to nanoparticles aggregation. There are few specific studies of their application in the conservation of architectural heritage field as this requires long-term durability tests and application on case-studies [5-6].

In order to improve these coatings, the synthesis of TiO₂ nanoparticles in benzyl alcohol was proposed so as to obtain pure anatase phase nanoparticles with an appropriate surface capping, which makes TiO₂ photo-active not only under UV light but also under solar light [7]. These innovative nanoparticles were tested, varying the type and concentration of their nano-dispersions, as conservation treatment for natural calcareous stones of different open porosity: Carrara marble, a metamorphic very compact stone, and Noto stone, a sedimentary, highly porous calcarenite. The effectiveness and durability of the treatments was evaluated according to standard protocols and by microscopic studies to assess the distribution of the nanoparticles on the stone surface.

2 Experimental Part

2.1 Materials and Methods

TiO₂ nanoparticles were synthesized according to the non-aqueous route, in which 4 mL of TiCl₄ (99.9 %, Sigma Aldrich) are slowly added to 80 mL of anhydrous benzyl alcohol (≥ 99.0 %, Sigma Aldrich) under stirring at room temperature. Benzyl alcohol was previously degassed under vacuum at 120 °C for 2 hours. Nanoparticles with the desired size were obtained using a reaction temperature of 80 °C and 24 hours reaction time. The resulting white suspension was centrifuged and washed three times, twice with ethanol and once with tetrahydrofuran. Finally the nanoparticles were added to water or ethylene glycol, in order to obtain dispersions with TiO₂ concentrations of 1 %, 2 % and 3 % by weight for water (WA) and of 1 %, 2 % and 4 % w/w for ethylene glycol (EG), identified by the codes WA1, WA2, WA3 and EG1, EG2, EG4 respectively.

For comparison, water dispersions of commercial nano-TiO₂ (TiO₂ P25, Evonik AEROXIDE®) were used. These nanoparticles are characterized by a crystalline composition with a ratio of 78:14:8 anatase–rutile–amorphous phase and the average sizes of the anatase and rutile elementary nanoparticles are 85 and 25 nm, respectively [8, 9]. This commercial titania was selected among different nano-TiO₂ available on the market because they are the most effective in terms of photocatalytic activity. The TiO₂ nanoparticles were added to water and sonicated for 15 minutes in order to obtain concentrations of 1 %, 2 % and 3 % by weight (codes CA1, CA2 and CA3, respectively).

The nano-TiO₂ dispersions were brushed on to the surface of the Noto stone and Carrara marble specimens. Two sizes were used: 50 x 50 x 10 mm and 50 x 50 x 20 mm, depending on the tests they would undergo. The specimens were washed with deionized water and dried to constant weight before treatment. Untreated stone specimens served as reference (REF) for comparison with treated ones.

The nanoparticle size and morphology were analysed using Transmission Electron Microscopy (TEM, Philips CM200-FEG) operated at 200 kV. The specimens for TEM analyses were prepared by depositing 1 drop of the water TiO₂ dispersion onto a carbon coated copper 200 mesh grid. The morphology of the stones before and after application of the treatments, as well as the penetration depth of the nano-TiO₂ were analyzed by Environmental Scanning Electron Microscopy (ESEM) and EDX analyses using a Zeiss EVO 50 EP microscope, equipped with an Oxford INCA 200 - Pentafet LZ4 spectrometer.

The color change of the surfaces, before and after treatment, was assessed by VIS spectrophotometric measurements, carried out with a Konica Minolta CM-600D instrument, with a D65 illuminant at 8°, wavelength range between 360 nm and 740 nm. Measurements were collected in the CIE L*a*b* standard color system, which describes a color with three different coordinates, L*, a*, and b*, measuring respectively brightness, red/green and yellow/blue color intensities. Ten measurements were performed on each area and the average results of L*a*b* were used to calculate the color difference ΔE^* between treated and untreated areas ($\Delta E^* = [(L^*_2 - L^*_1)^2 + (a^*_2 - a^*_1)^2 + (b^*_2 - b^*_1)^2]^{1/2}$).

The photocatalytic activity of TiO₂ nanoparticles was verified by means of the decomposition of an organic colorant (Rhodamine B (rB) in aqueous solution 0.050 ± 0.005 g/l) test, both after indoor exposition of the treated specimens and after ageing in a solar box with a Xenon lamp. The Rhodamine B solution was applied to the surface of both untreated and treated specimens (1 ml per specimen), then, after drying, colorimetric measurements were carried out as described above. The degradation of the applied organic dye was monitored by evaluating the color change of the surfaces exposed indoors 70 cm from a window with east exposure in Milan from September to March after 1, 17, 26, 120, 312, 528, 696, 1968 and 4128 h. The degradation of Rhodamine B was also evaluated on specimens aged in a solar box, Suntest CPS+ equipped with a Xenon arc lamp source and a cut off filter for wavelengths below 290 nm. The irradiation was kept constant at 765 W/m^2 , at a distance of 20 cm at constant temperature of 35 °C. The aim of the test was the photoactivity evaluation of TiO₂ under solar irradiation. In order to better simulate the real condition of treated and outside exposed stones, it was decided to use a Xenon lamp, instead of an UV lamp, because it has a spectral emission similar to that of solar light. The color changes of the surfaces were monitored after 15, 30, 60, 90 and 150 minutes of irradiation. Only the chromatic coordinate a* was used to evaluate the photocatalytic discoloration of the stain over time ($D^* = (|a^*(t) - a^*(rB)| / |a^*(rB) - a^*(0)|) * 100$, where a*(0) and a*(rB) are the average values of chromatic coordinate a* before and after the application of the stained solution and a*(t) is the a* value after t hours of light exposure).

Static contact angle and capillary water absorption tests were carried out in order to evaluate the changes of the wettability and water absorption of

the stone surfaces after the application of the nano-TiO₂ dispersions. The static contact angle test was performed on 15 points for each specimen, according to UNI standard protocol [10], using an OCA (Optical Contact Angle) 20 PLUS (DataPhysics, Germany), with a drop volume of 5 μl , after 10 seconds. Drop shape was recorded with a camera and the angle between the substrate surface and the tangent from the edge to the contour of the water drop (contact angle) was evaluated. The capillary water absorption of the stone specimens before and after the application of the treatments was performed according to UNI standard protocol [11] on 50x50x20 mm specimens of both Noto stone and Carrara marble. This test consists in the determination of the capillary water absorption of the specimen in contact with deionized water. The capillary water absorption value per unit area (Q_i , expressed in mg/cm^2) is defined with this formula: $Q_i = (m_i - m_0) / A * 1000$, where m_i is the mass (g) of the wet specimen at time t_i , m_0 is the mass (g) of the dried specimen, A is the surface area (cm^2) in contact with the water. The specimens were weighed at the following time interval: 10 min, 20 min, 30 min, 60 min, 4 h, 6 h, 24 h, 48 h.

Finally, to assess the durability of the treatments, some specimens were exposed outside, in Milan, on the roof of a building, at 45°, facing west, for nine months, from September to June. The color changes of the surfaces were monitored monthly using a VIS spectrophotometer as previously described. In particular the variation of the parameters L* ($L^* = L^*_i - L^*_0$, where L^*_i is the L* value at time t_i and L^*_0 is the L* value at time t_0) and b* ($b^* = b^*_i - b^*_0$, where b^*_i is the b* value at time t_i and b^*_0 is the b* value at time t_0) in time were monitored.

3 Results and Discussion

3.1 Characterization of TiO₂ Dispersions

To study size and morphology of the synthesized TiO₂ nanoparticles, the water TiO₂ dispersions at 3 % w/w concentration were observed with TEM. As shown in Fig. 1, it is possible to identify the presence of primary nanoparticles of anatase of about 5–6 nm, aggregated in elongated structures whose the longest axis measures about 40 nm. Moreover, these structures do not further aggregate in the dispersion but show a homogenous distribution.

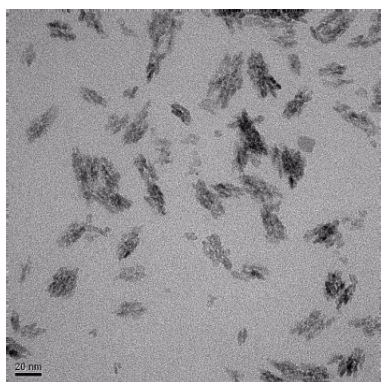


Figure 1: TEM image of 3 % w/w water TiO₂ nanoparticles.

3.2 Evaluation of the Effectiveness of the Treatments

In order to evaluate the maintenance of the aesthetic properties of the stones after the application of the synthesized TiO₂ dispersions, colorimetric tests were performed. The results, in terms of ΔE^* values for each treatments (WA1, WA2, WA3, EGA1, EGA2, EGA4, CA1, CA2, CA3) and for each substrate are reported in Table 1.

As shown, ΔE^* values for Noto stone specimens treated with the commercial water dispersions of nano-TiO₂ at 2 % and 3 % w/w (CA2, CA3) are far higher than 5, the acceptable limit of ΔE^* value for restoration treatments in the field of cultural heritage. Therefore they are not suitable for restoration purpose and for this reason, only the CA1 treatment with commercial nano-TiO₂ at 1 % w/w was used to be compared with the other tests. For the Noto stone, after the application of the new treatments, ΔE^* values are lower than 0.69 ± 0.56 , while for Carrara marble the ΔE^* values are lower than 1.35 ± 0.91 . The obtained results show that the nano-TiO₂ treatments do not modify the original color of the stone sur-

faces, since color variations with ΔE^* values lower than 1 are not visible to naked eye.

The photocatalytic properties of the new TiO₂ dispersions were evaluated with the Rhodamine B test, both after indoor exposition of the treated specimens and after ageing in solar box with a Xenon lamp.

The fading of the organic colorant was monitored by color measurements over time and the values of discoloration D^* ($D^* = (|a^*(t) - a^*(rB)| / |a^*(rB) - a^*(0)|) * 100$) as a function of exposure time (h), are shown in Fig. 2. The D^* values show a greater slope in the first hour of exposure, then the values reach a plateau because the degradation kinetics of the red dye slows down. It should be noted that the reference D^* values also increase with time, probably because of the direct effect of the light on the degradation of the dye, however D^* values of the treated specimen are always higher than those of the reference specimen, because the presence of nano-TiO₂ accelerates the dye degradation. For instance, in the first hours of exposure the ratio between the D^* value of the specimens treated with EGA4 and those of the reference is about 2.74 while at the end of the test is 1.38. For the case of the treated specimens, at equal exposure times, those treated with nano-TiO₂ dispersions in ethylene glycol (EGA2 and EGA4) show better performance than those treated with nano-dispersions in water. By the end of the test the differences between the most concentrated can be considered negligible.

Two equivalent sets of treated Noto stone and Carrara marble specimens were artificially aged in a solar box equipped with a Xenon lamp, in order to have a faster evaluation of the photocatalytic activity of the specimens. The results obtained are

Table 1: ΔE^* values of Noto stone and Carrara marble specimens before and after the application of TiO₂ treatments.

			ΔE
	Solvent	Nano-TiO ₂ concentration (w/w)	Noto stone
WA1	Water	1 %	0.12±0.08
WA2	Water	2 %	0.40±0.12
WA3	Water	3 %	0.16±0.01
EGA1	ethylene glycol	1 %	0.22±0.02
EGA2	ethylene glycol	2 %	0.33±0.12
EGA4	ethylene glycol	4 %	0.69±0.56
CA1	Water	1 %	3.60±1.40
CA2	Water	2 %	8.73±3.49
CA3	Water	3 %	8.91±3.61

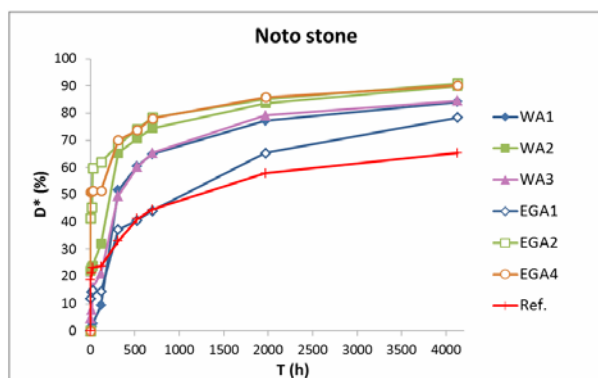


Figure 2: Stain discoloration values D^* (%) as a function of time (h) for Noto stone specimens after indoor exposition to solar light.

shown in Fig. 3 and, similarly to the previous test results, the stain discoloration D^* values increase faster during the first minutes of light exposition. For the Noto stone, the best results were achieved for specimens treated with the highest TiO₂ concentration dispersions (WA3 and EGA4), whereas in the case of the Carrara marble the highest effectiveness was achieved by specimens with ethylene glycol nano-TiO₂ dispersions, particularly EGA4. Comparing the stain discoloration curves for both stones it is clear that the discoloration D^* of the dye is much faster on marble specimens being almost 70 % while for the Noto stone it is 38 % during the first 15 minutes. This could be explained by the fact that a lower concentration of nano-TiO₂ is present on the surface of the Noto stone specimens as it is a more porous stone allowing the penetration of the nanoparticles into the substrate.

The D^* values of the treated specimens are higher than the ones for the references. This indicates that the nano-TiO₂ dispersions are able to accelerate the degradation of the soiling, in agreement with the

results obtained by indoor exposure of the specimens to solar light (Fig. 2). As shown in Fig. 3, the innovative water and ethylene glycol TiO₂ dispersions are more effective than commercial titania treatments in terms of photocatalytic activity, even if in the first minutes the commercial nanoparticles are more photocatalytic than the reference, at the end of the test they reach quite the same value of stain discoloration D^* (about 60 %), especially in Carrara marble specimens.

In order to evaluate the effect of the application of nano-TiO₂ treatments on the surface wettability of the two stones, static contact angle measurements were carried out since these treatments are known to improve the wettability of the surfaces and therefore it is important to quantify this aspect. In the case of the Noto stone, because of its high open porosity and roughness, it was not possible to carry out the measurements (water drop is lost within the first 10 seconds). The values of static contact angles for treated and untreated Carrara marble specimens are presented in Fig. 4. The contact angle values of the specimens treated with water and ethylene glycol dispersions are lower than those of both reference specimens (REF is the untreated marble and REF_EG is the marble treated with the ethylene glycol solvent). This means that the new synthesized nano-titania slightly alters the wettability, making the stone surfaces more hydrophilic than the references, thus hopefully improving the self-cleaning properties. Fig. 4 also shows that specimens treated with the water dispersion of commercial nano-TiO₂ (CA1) show a higher static contact angle value than the untreated reference specimen (REF) being similar to that of the reference specimen treated with ethylene glycol

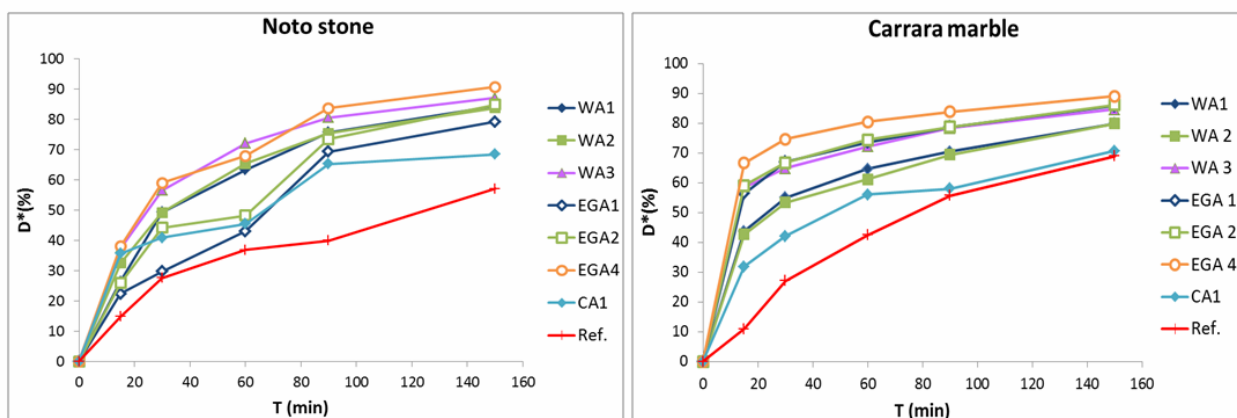


Figure 3: Stain discoloration values D^* (%) as a function of time (h) for Noto stone (left) and Carrara marble (right) specimens after artificial ageing in solar box.

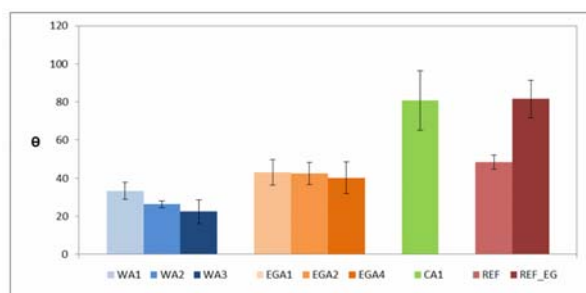


Figure 4: Contact angle values of Carrara marble specimens, treated with new synthesized titania treatment (WA1, WA2, WA3, EGA1, EGA2, EGA4), with commercial titania (CA1), untreated reference (REF) and reference treated with ethylene glycol (REF_EG).

(REF_EG). The commercial treatment does not achieve the same surface hydrophilicity as the synthesized titania-water treatments (WA1). This should be related to the fact that without UV irradiation, the commercial nano-TiO₂ does not show photo-induced hydrophilic properties, while the new synthesized nano-TiO₂ is photo-active also under usual natural light exposure. Moreover, the standard deviations of these values are higher than the others, indicating that the surface properties are inhomogeneous. This could be attributed to the aggregation of commercial nanoparticles that leads to an irregular distribution of nanoparticles and to an increase of the roughness of the stone surface.

Capillary water absorption curves for both Noto stone and Carrara marble specimens were carried out before and after the application of the synthesized and commercial nano-TiO₂ treatments. The results show that there is no significant difference between the curves measured before and after the application of nano-TiO₂ dispersions. The Q_1 values differ among the specimens because of physical properties such as porosity rather than because of the nano-TiO₂ nature of the treatments. This confirms that the presence of nano-TiO₂ does not alter the water absorption by capillarity of these materials. The only exception occurs for Carrara marble specimens treated with ethylene glycol TiO₂ dispersions that seem to show a slight reduction in the water absorption (Fig. 5).

3.3 Evaluation of the Penetration Depth of Titania Treatments

The surface and cross-section of the both untreated and treated specimens of the two stones were analyzed by SEM-EDS, in order to study the morphological surface changes and the penetration depth of the titania nanoparticles. The distribution of new water and ethylene glycol nano-TiO₂ dispersions on Noto stone surfaces was not homogeneous,

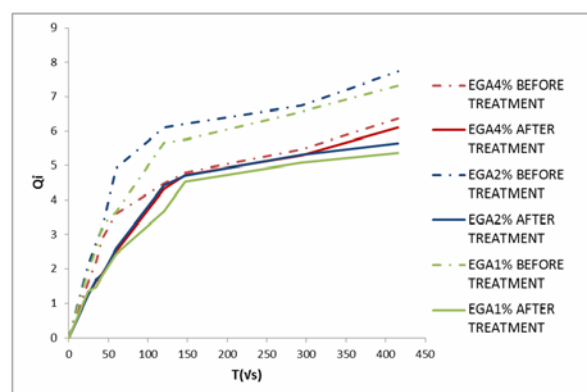


Figure 5: Water absorption by capillarity before (dashed lines) and after (solid lines) the application of the titania ethylene glycol dispersions on Carrara marble.

because the physical features of the stone (porosity, roughness) lead to the aggregation of the titania mostly within pores, even in depth (Fig. 6). On the contrary, on Carrara marble specimens, the treatments create a continuous and homogeneous nano-TiO₂ layer on the surface (Fig. 7). The commercial water dispersion (CA1) treatment forms aggregation of nanoparticles on the surfaces of both types of stone specimens and the Ti concentration in this case is much lower (Fig. 8).

Observation of the specimens in cross-sections show that on Carrara marble specimens the new treatments were present only within the first few microns, whereas the penetration depth in Noto stone ranged between 300-500 μm because of its porosity so that the nanoparticles penetrate into the specimen reducing their amount on the surface. A possible way to prevent the penetration of TiO₂ nanoparticles into porous substrates could be to apply the titania dispersions after a pre-treatment with a consolidant. To evaluate this solution, some tests are currently in progress.

3.4 Evaluation of Outdoor Environment Photocatalytic Activity

Some stone specimens treated with the new synthesized nano-TiO₂ dispersions and reference specimens were exposed outside in Milan for 9 months in order to study the photocatalytic and self-cleaning activity that would reduce the deposition of particulate matter (solid inorganic particles, dust like inorganic compounds, fly ashes and elemental carbon) and their durability in an urban polluted environment.

Figures 9 and 10 show the ΔL^* and Δb^* values measured each month for both the Noto stone and Carrara marble, respectively. The data for Δa^* are not shown because their variation over time is neg-

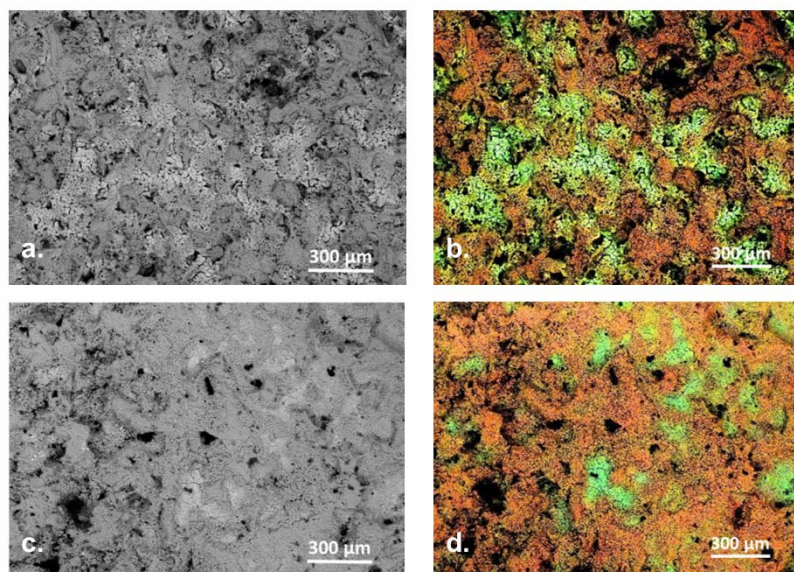


Figure 6: ESEM-EDX characterization of the Noto stone surface treated with WA3 (a.), and EGA4 (c.). False color images indicate the distribution of titanium (green) and calcium (orange) (b.-d.).

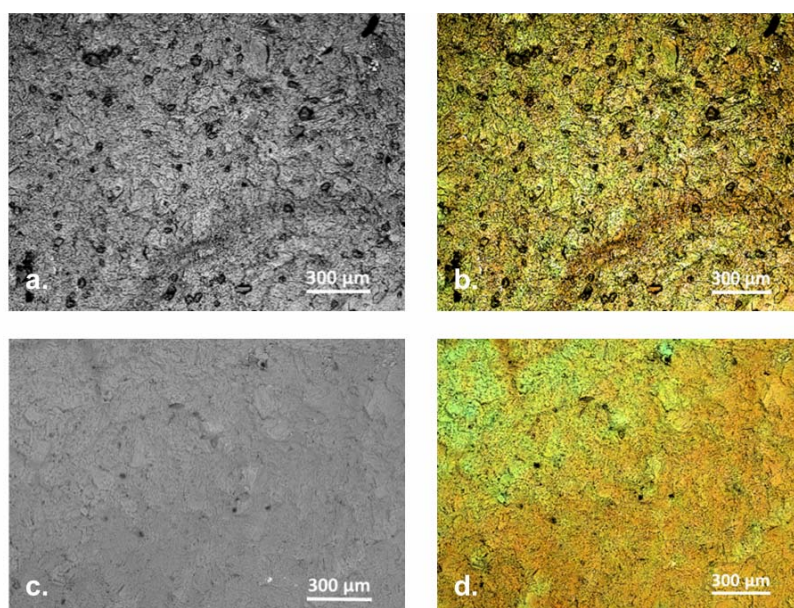


Figure 7: ESEM-EDX characterization of the Carrara marble surface treated with WA3 (a.), and EGA4 (c.). False color images indicate the distribution of titanium (green) and calcium (orange) (b.-d.).

ligible. In general, by observing the ΔL^* curves for both substrates, it is possible to notice a general brightness decrease related to the deposition of atmospheric soil, especially during winter months, whereas brightness increases can be ascribed to the cleaning effect of meteoric water. The Δb^* values for the Noto stone specimens decrease with time, indicating a decrease of the yellow component of color, while for Carrara marble specimens an increase in the yellow component was observed.

For Noto stone specimens, the nano-TiO₂ treated specimens do not show any relevant improvement in the inhibition of accumulation of soil (Fig. 9),

compared to the reference, that can be explained by the penetration of the nanoparticles into the porous stone thus reducing the amount left on the surface. For treated Carrara marble specimens, the nano-TiO₂ coatings lead to a decrease of the accumulation of dirt and pollutants on the surface compared to the reference, as the ΔL^* data are slightly lower (Fig. 10). Regarding the Δb^* curves, in the testing period one could notice some yellowing not affected by the presence of nanoparticles treatments. WA2 treatment is not reported as it showed an abnormal behavior, which could not be explained requiring further investigations.

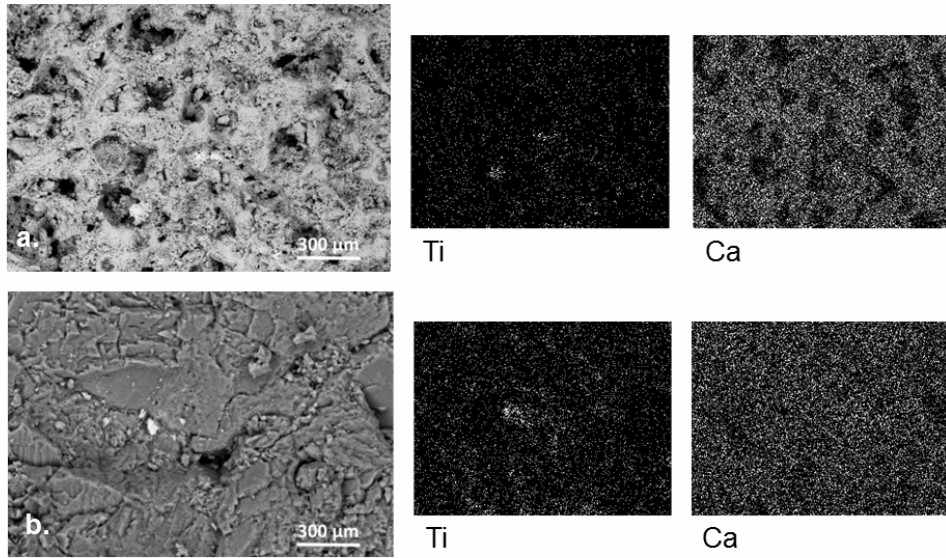


Figure 8: ESEM-EDX characterization of the Noto stone (a.) and Carrara (b.) marble surface treated with CA1 and grey scale images of distribution of titanium and calcium.

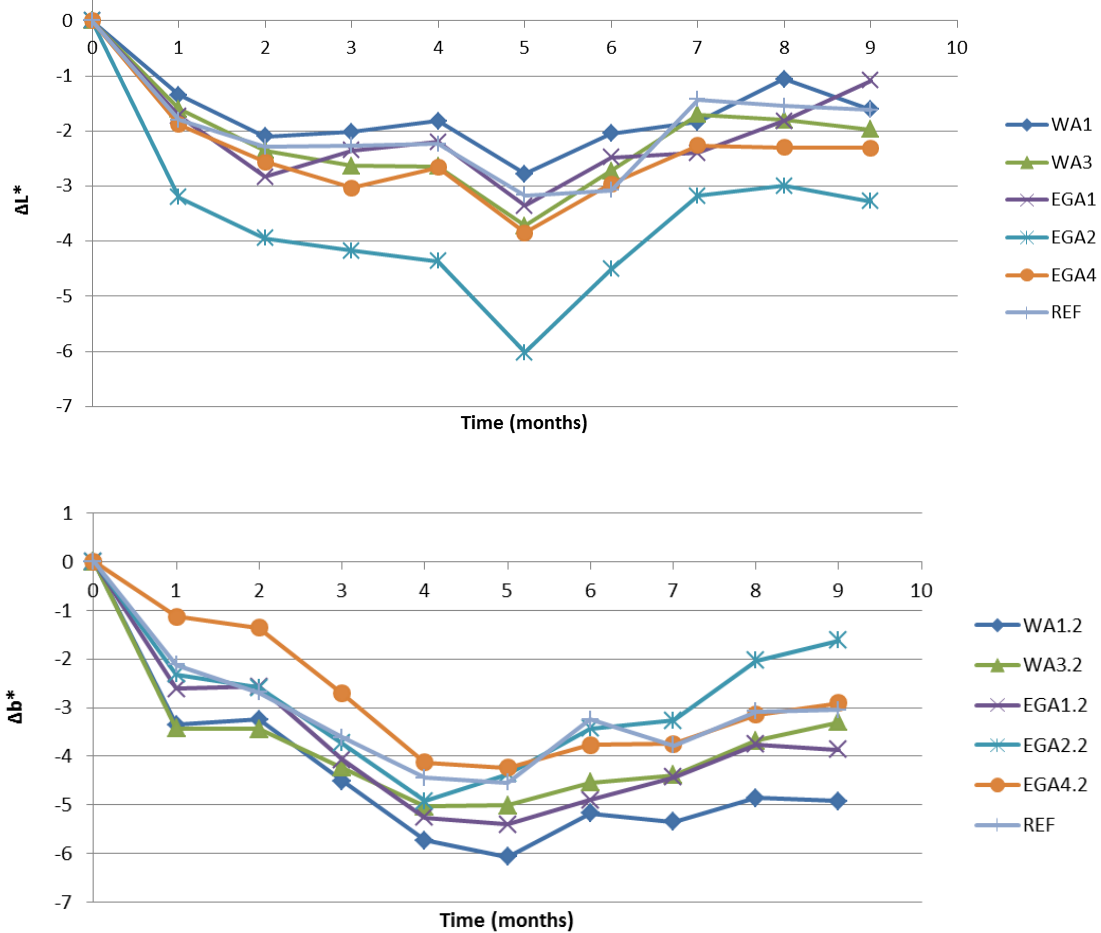


Figure 9: ΔL^* and Δb^* curves of Noto stone specimens exposed in outdoor conditions in the polluted Milan atmosphere.

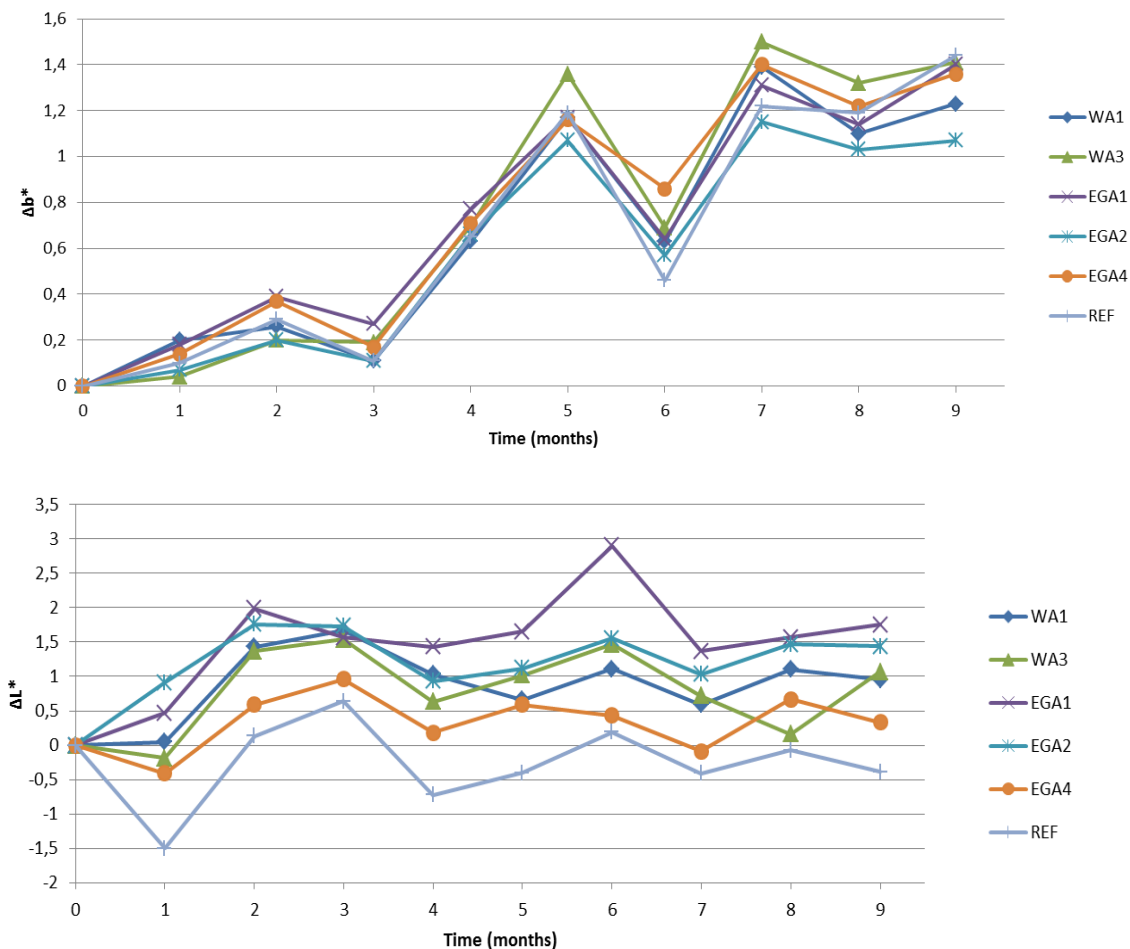


Figure 10: ΔL^* and Δb^* curves of Carrara marble specimens exposed in outdoor conditions in the polluted Milan atmosphere.

4 Conclusions

The study focused on new photocatalytic treatments based on water and ethylene glycol dispersions of benzyl-capped anatase nanoparticles at different concentrations, applied onto Noto stone and Carrara marble specimens. The effectiveness and photocatalytic activity of these new treatments were also evaluated by comparison with water commercial dispersions of titania nanoparticles.

Regarding the photocatalytic activity, the results showed that the synthesized titania nanoparticles are photoactive not only under UV light but also under solar light and therefore are more effective than commercial titania when applied outdoors. These treatments do not significantly alter the aspect and water absorption properties of the considered stones.

Color change evaluations carried out on specimens exposed outdoors to weathering showed that treated Carrara marble specimens have a self-cleaning effect compared to the untreated reference specimen. On the other hand, treated Noto stone specimens are less effective in preventing soiling because of the increased nanoparticle penetration into the porous substrate. These photocatalytic materials are suitable for historical building maintenance purposes because they promote the degradation of polluting organic agents. After further studies and an improvement of treatment methodology they could be effective against soiling both in the case of compact and porous stone substrates. They are promising in that these types of treatments could reasonably limit the frequency of extraordinary conservation interventions of architectural heritage, thus decreasing maintenance costs.

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